Kinetics of Pd supported on swellable organically modified silica (SOMS) catalysts during aqueous phase hydrodechlorination of trichloroethylene

Undergraduate Thesis

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Abstract

The past few decades have seen a rise in concern regarding environmental issues prompting many areas of research to find efficient means of breaking down hazardous chemicals used in manufacturing and industrial centers. One such hazardous chemical, trichloroethylene (TCE) has been a major concern due to its toxicity and pollution of drinking water sources such as groundwater. Currently, hydrodechlorination (HDC) over noble metal-based catalysts is employed in the conversion of TCE into benign products, such as ethane. However, in addition to producing ethane, this conversion of TCE molecules also produces hydrochloric acid (HCl) as a byproduct, which is known to deactivate noble metal catalysts. In order to circumvent this issue, our group has been exploring a novel catalyst support known as SOMS (swellable organically modified silica) which prevents deactivation of noble metal sites by HCl due to its hydrophobicity and swellability [1]. While kinetics for the HDC of TCE has been established in literature for many conventional supports prior, only recently have the kinetics of the HDC of TCE been explored for animated supports such as SOMS [2]. However, the effect of particle size of noble metal particles embedded within SOMS on the HDC of TCE has not yet been explored. This research project investigates the effect of size of palladium (Pd) nanoparticle sites embedded within the SOMS matrix on the kinetics of the HDC of TCE.

Acknowledgments

I would first and foremost like to thank Dr. Umit Ozkan for welcoming me into the Heterogeneous Catalysis Research Group as a freshman undergraduate student those many years ago. As a result of all my mentors and graduate students I've worked with over the years, most recently and most importantly to this project Anagha Hunoor and Saurabh Ailawar, this group has become more of a family to me than nearly anything I've ever had to date. My hope is that from the lessons I've learned from you all, as well as within the William G. Lowrie Department of Chemical and Biomolecular Engineering, that I will make an excellent graduate student and even better researcher.

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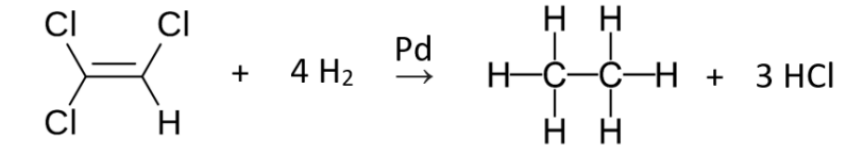
Introduction

Background

Trichloroethylene (TCE) is used as a solvent in a wide variety of industrial applications and has recently attracted the attention of many chemical regulatory bodies due to its presence in a major source of drinking water: groundwater [3-6]. While the severity of effects depends on length and type of exposure, side effects of exposure to TCE in humans includes numbness, weakness, central nervous system (CNS) related degradation, and even various types of cancer [7]. As of 2010, a report by the U.S E.P.A. found an annual release of TCE equal to 2.3 million pounds into the environment, as well as its presence in groundwater and soil above the 5 μg/L safety threshold at 700 of 1300 hazardous waste sites analyzed [8]. Currently, a method that is being considered for the transformation of TCE into harmless components is a chemical reaction known as hydrodechlorination (HDC) [9-10]. HDC is being considered as an alternative to traditional physical separation methods such as adsorption and stripping towers due to its separation efficiency and ease of compliance with EPA regulatory standards [7]. As well, HDC carries benefits over traditional methods in that it completely eliminates TCE rather than transferring it into another phase for handling [7]. The HDC reaction, as seen below in Equation 1, involves TCE reacting with hydrogen over a noble metal catalyst which helps strip the chlorine atoms away from TCE, reducing it in solution to ethane.



Trichloroethylene Ethane (1)

Regarding the noble metal catalysts used in the HDC of TCE, some of the commonly used metals include Pt, Ru, Au, and Pd. Of this list, Pd is among the most widely used in industrial applications [11]. Typically, these noble metals are dispersed onto supports to provide mechanical stability and enhance interaction with the molecules undergoing the HDC reaction. Conventionally used supports for metal-based catalysts include silica, alumina, and carbon-based materials [11]. However, noble metal catalysts with conventional supports, such as Pd supported on alumina or silica, used in the HDC of TCE suffer from deactivation by chloride species formed as a byproduct of the reaction [1]. During deactivation, the chloride species adsorb onto the active sites of the noble metals like Pd and block the sites for the reaction [1]. While many mechanisms have been proposed to stave off long-term inhibition, recently, a novel, animated material known as swellable organically modified silica (SOMS) has been utilized by our group as an alternative catalyst support [1,12-13]. SOMS is a novel material consisting of a highly crosslinked network of bridged polysilsesquioxanes that has the ability to swell up to three times its original volume in the presence of organic solvents such as acetone, ethanol, and TCE [14]. The swellability of SOMS enables the placement of noble metal catalyst sites, such as Pd, into the interior of the pores of the material. Additionally, the hydrophobicity of SOMS aids in repelling species that would deactivate the Pd surface such as sulfides and chlorides, thus protecting the Pd particles as can be seen in Figure 1 [13]. This has been demonstrated to hold true in our prior research which shows that Pd sites placed within a SOMS matrix show a significant resistance to deactivation by chloride species as compared to conventional, non-animated catalyst support such as alumina [13].

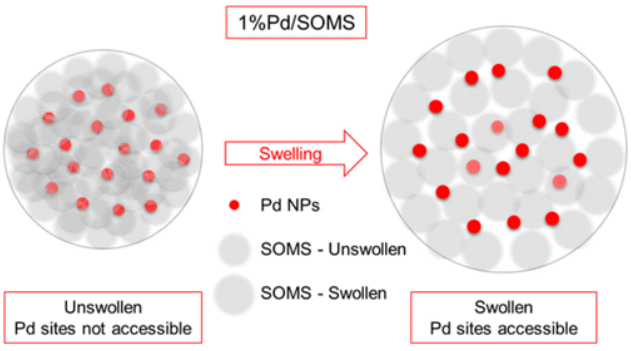


Figure 1: Demonstration of how the swelling mechanism of SOMS can regulate accessibility of Pd sites. [13]

While the novel properties of SOMS are beneficial in improving catalyst resistance to deactivation by HDC byproducts, they also present unique challenges with respect to characterization techniques and kinetic explorations. The swelling mechanism, specifically, poses difficulties with respect to characterization of active sites located in the pores of SOMS using traditional techniques such as X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM) as they don't easily accommodate saturation of the pores of SOMS with organic solvents [2]. While the kinetics of the HDC of TCE has been more thoroughly explored on conventional supports, kinetics of this reaction for Pd/SOMS has been recently reported by our group [2]. However, two kinetic quantities that were not explored in this study were the turnover frequency and rate of reaction.

In catalysis, the rate of reaction under various reaction conditions is one of the most studied aspects of any reaction. Turnover Frequency (TOF) is one such kinetic quantity that helps in determining the rate at which reactions occur, but as a function of the available active sites on the catalyst used in the reaction. As well, TOF also helps in creating a standard of comparison which can be used to compare the activity of catalysts and determine their efficiency. As seen in Equation 2, below, TOF is defined as the number of moles of products (n) formed per unit time, per moles of available, active catalyst sites (S) [15]:

$$v_t = N(s^{-1}) = \frac{1}{S}(\frac{dn}{dt}) \quad (2)$$

As seen in the in the TOF equation, the (dn/dt) term refers to the rate of reaction. Often expressed on its own outside of the TOF equation, the rate of reaction is a measure of the change in the concentration of reaction species per unit time. This is often represented as a function of a rate constant multiplied by the concentration of various chemical species each raised to a power known as their respective 'order'. The order of reaction for a chemical species demonstrates how strongly

it influences the overall rate of reaction. For example, in Equation 3 below, the terms [A] and [B] denote the concentrations of reactants A and B with x and y as their respective orders. The k term is simply a constant known as 'rate' constant.

$$\left(\frac{dn}{dt}\right) = k[A]^x[B]^y \quad (3)$$

In the literature available on the HDC of TCE for conventional supports, some studies have reported on the rate of reaction as well as the turnover frequency. With respect to rate of reaction, some studies have reported the rate to be first order in TCE and zero in H_2, making it a pseudo-first order reaction [16], whereas other studies have demonstrated the rate to not be necessarily first order, but rather highly dependent on the concentration of TCE present [17]. With respect to turnover frequency, studies have reported it to vary as a function of both catalyst particle size as well as concentration of product chloride species concentration [18-19]. As well, difficulties in properly calculating TOF as a result of porosity of traditional supports has also been shown in literature [20]. However, as stated above, no explorations of these values have yet been undertaken with respect to an animated support such as SOMS.

Research Significance

While the kinetics of HDC of TCE on Pd-SOMS has been recently explored, difficulties with syntheses and standard characterization techniques have further limited exploration of kinetic quantities such as TOF and rate of reaction. Additionally, no syntheses specifically aimed at controlling the size of Pd sites entering the SOMS matrix have yet been explored. Thus, the significance of this study is that it first aims to adapt a synthesis methodology in order to control the size of the Pd sites located within the pores of SOMS. After accomplishing such, this study

will then attempt to determine the TOF and rate of reaction of the HDC of TCE as a function of size of Pd sites within SOMS.

Overview of Thesis

In order to overcome the gap in understanding of the kinetics of HDC of TCE on Pd SOMS, size controlled Pd nanoparticles were first synthesized within the SOMS matrix. Post-synthesis, the nanoparticles were characterized with several techniques, including inductively coupled plasma – optical emission spectroscopy (ICP-OES), X-Ray photoelectron spectroscopy (XPS), and N_2 Physisorption with BET and BJH methods. Once these characterization tests were completed, multiple stages of kinetic tests were completed carrying out the HDC of TCE under various starting conditions. The results from these tests were then used to determine the rate of reaction for the HDC of TCE as well as the kinetic quantities needed to find the TOF.

Methodology

Synthesis

In order to synthesize Pd-SOMS catalysts with varying sizes of Pd catalyst sites, we used a modified synthesis technique from Teranishi, et al. which uses different ratios of Pd to polyvinylpyrrolidone (PVP). In this synthesis, PVP acts as a capping agent which binds to Pd to control the size of Pd nanoparticles made in reflux [21]. This modified synthesis technique consisted of a one pot reflux setup with 29 mL of toluene, 21 mL of ethanol, 0.1347 g. of palladium acetate, 0.1347 g. of PVP, and 1 g. of as-delivered SOMS. This reflux solution would be constantly stirred at 100 ^{o}C for 3 hours. The final reflux solution was filtered and then washed 10 times with 20 mL of ethanol, with both the initial reflux filtrate and subsequent washes being collected for later analysis. After filtering, the Pd-SOMS powder was dried in an oven overnight at 60 ^{o}C. The finished catalyst was then recovered and stored for characterization and catalytic testing.

In order to vary the size of the Pd sites made via this synthesis technique, the weight ratio of palladium acetate to PVP was changed. While the aforementioned numbers, thus, refer to the 1:1 palladium acetate to PVP synthesis technique, 0.1:1 and 10:1 samples were also synthesized using 0.01347 g. and 1.347 g. of PVP, respectively. These samples will simply be referred to by their respective PVP:Pd weight ratios from here on.

Catalyst Characterization

As a result of the novelty of the synthesis technique used to make the Pd-SOMS samples in this study, several physical characterization techniques were employed to study the samples. First, ICP-OES was conducted to determine the weight loading of Pd within each sample. Then, N_2 Physisorption and XPS were conducted on each of the samples in order to determine the location of Pd within each sample.

ICP-OES

The amount of Pd remaining in the filtrate and wash solutions after synthesis were analyzed by ICP-OES. After the syntheses were complete, the wash and filtrate solutions were filtered using a syringe filter and then subjected to elemental analysis in order to find the concentration of Pd in solution. This analysis was carried out using a Perkin-Elmer Optima 4300DV ICP-OES instrument.

XPS

The XPS spectra of the 0.1:1, 1:1, and 10:1 samples were acquired using a Kratos Ultra Axis Spectrometer equipped with a monochromatized Al Kα X-Ray source operating at 12 kV and 10 mA. Each of the samples were loaded on to carbon tape and placed in the XPS chamber which was evacuated overnight. After evacuation, a survey scan followed by high resolution region scans were collected with the charging effects being corrected with respect to C 1s (284.5 eV). The atomic ratios of elements on the surface of the sample were calculated after correcting the XPS signal intensities via atomic sensitivity factors via CasaXPS software.

N_2 Physisorption

The surface area and pore volumes of each of the samples were analyzed via a Micrometrics accelerated surface area and porosimetry instrument (ASAP 2020). Prior to analysis, the samples

were degassed at 120 ^{o}C under a vacuum of 2 μmHg to rid the samples of adsorbed gases and moisture. The surface area of each of the samples was determined using Brunauer-Emmett-Teller (BET) method while the pore volume of the samples was determined using Barrett-Joiner-Halenda (BJH) method.

Kinetic Testing

The kinetic testing carried out for the aqueous phase HDC of TCE using the various Pd-SOMS samples was conducted in a flow reactor setup in which a solution of TCE in methanol and hydrogenated water are combined and passed through a bed of Pd-SOMS catalyst. The resulting chloride species created from this reaction at the catalyst bed was then measured via a Pharmacia Biotech conductivity meter. The readings from the conductivity meter, which were read throughout the run time of the experiment, were then converted into percent yield of HCl. Percent yield of HCl is defined as the moles of HCl formed as compared to the maximum moles of HCl that could be formed via complete dechlorination of all available TCE molecules. For all experiments, a fixed amount of 30 mg of Pd-SOMS catalyst was used. Unless otherwise stated, 5000 PPM TCE in methanol solution was introduced into the flow reactor system using a New Era pump system. The hydrogenated water used in the system was created by bubbling pure hydrogen through 1 L of deionized water for an hour and a half immediately prior to the experiment. The hydrogenated water was pumped into the flow reactor system using an ISCO syringe pump.

Two sets of kinetic tests were done on each of the aforementioned Pd-SOMS samples synthesized. The first set of experiments were done in order to determine the steady state yield of HCl for the turnover frequency of the HDC of TCE reaction over each Pd-SOMS sample. For this set of

experiments, each sample received three runs in the flow reactor setup with the hydrogenated water solution containing 0%, 5%, and 10% ethanol substitutions in order to find the steady state yield of HCl at various levels of swelling of the SOMS matrix. The second set of experiments that were conducted were done to determine the rate order of each of the reactants in the HDC of TCE as well as the rate constant. For this set of experiments, each sample first received two runs in the flow reactor with the TCE-methanol solution having 5000 PPM and 10000 PPM TCE in order to determine the rate order for the HDC reaction with respect to TCE. Then, each sample received two runs in the flow reactor with the hydrogenated water solution having 1.5 hours and 0.5 hours of pure hydrogen bubbling in order to determine the rate order for the HDC reaction with respect to hydrogen.

Results

Synthesis

In order to synthesize Pd-SOMS catalysts with varying sizes of Pd sites, the initial synthesis technique used was adapted from Li, et al. which used different lengths of time of reflux to control the size of catalyst sites [22]. This modified synthesis technique consisted of a one pot reflux setup with 29 mL of water, 21 mL of Ethanol, 0.1347g of palladium acetate, and 0.667g of PVP. The reflux solution was then constantly stirred at 120 ^{o}C for a variable length of time, in which time of reflux and Pd site size were directly correlated. The final reflux solution was then collected and excess solvent was evaporated from the solution overnight at 70 ^{o}C. Once dried, the Pd nanoparticle powder was then collected and impregnated into the SOMS matrix via a wetness impregnation technique. However, several challenges were faced with this synthesis. First, for longer running reflux times which were used to produce larger Pd nanoparticles, the nanoparticles were found to agglomerate post-evaporation both in and out of a solution that would be used to resuspend them. Additionally, for shorter running reflux times which were used to produce smaller Pd nanoparticles, issues were faced in recovering the Pd nanoparticles from solution as well as impregnating them within the SOMS matrix.

Due to the issues faced within this synthesis technique, we chose to change our procedure to a modified synthesis technique from Teranishi, et al., in which the ratio of PVP to Pd was varied in order to produce differing Pd nanoparticle sizes, rather than the reflux time [21]. Additionally, we modified the synthesis technique to include SOMS in the one-pot reflux setup in order to help circumvent potential issues with post-reflux nanoparticle recovery and storage. Ultimately, success was found with this synthesis technique as outlined in the Methodology section, and we were able

to synthesize three different samples: 0.1:1, 1:1, and 10:1. Each of these samples were assigned a name based on the ratio of PVP:Pd in their respective reflux setups. Increasing the ratio of PVP:Pd was expected to correlate to a decreasing Pd catalyst site size in the final synthesized product.

Catalyst Characterization

Several characterization techniques were employed to study the effect of varying the ratio of PVP:Pd on the catalyst samples. First, ICP-OES was performed on the filtrate and wash solutions collected during synthesis. This concentration of Pd obtained in the above-mentioned solutions was subtracted from the known initial weight of Pd put into each synthesis, and the amount of Pd remaining adhered to the SOMS matrix was then back calculated. The results of these calculations may be found below in Table 1.

Table 1: ICP-OES results and determined weight percentage of Pd in each sample.

	PVP : Pd Ratio	0.1 : 1	1 : 1	10 : 1
Filtrate	(µg/mL)	332	479	448
Wash	(µg/mL)	3.98	8.96	11.94
Filtrate	Total mg	16.61	23.95	22.42
Wash	Total mg	0.72	1.61	2.15
Total wt%		1.74	1.62	1.64

As observed in Table 1, the 1:1 and 10:1 samples were found to have very similar weight loadings of Pd at 1.62 wt% and 1.64 wt%, respectively. However, the 0.1:1 sample had a noticeably higher weight loading of Pd at 1.74 wt%. Due to this relatively large difference in 0.1 wt% loading, as well as focusing on the change in kinetics of the HDC of TCE as a function of particle size rather than catalyst loading, we chose to not use the 0.1:1 samples for kinetic testing experiments.

Next, XPS was done on each of the samples in order to quantify the amount of Pd sites located on the surface of each sample. Shown in Figure 2 are the combined XPS scans for the Pd 3d region of the 10:1, 1:1, and 0.1:1 samples. Table 2 contains the area under the curve for each of the samples as well as the ratios of Pd/Si on the surface area scanned for each sample. As shown, a decrease in the ratio of PVP to Pd is tied to an increased area under the curve for the Pd 3d region as well as a decreased ratio of Pd to Si at the surface of the tested samples.

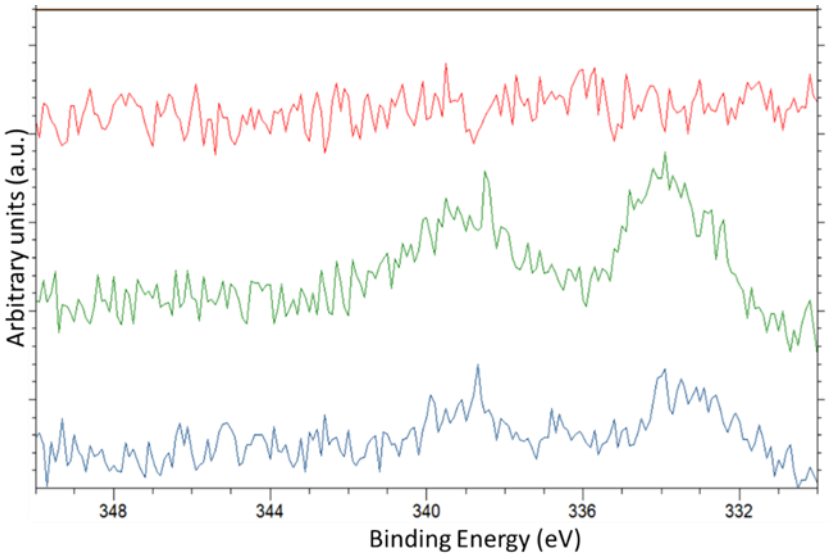


Figure 2: XPS scan results for the 10:1 (Red), 1:1 (Blue), and 0.1:1 (Green) samples.

Table 2: Numerical data collected from XPS scan results of Figure 2.

PVP : Pd	Area Under Curve		Pd/Si
Ratio	Pd 3d	Si 2p	Surface Ratio
10 : 1	13.8	236.2	0.058
1 : 1	51.9	236.3	0.22
0.1 : 1	127.5	233.9	0.545

Since it was believed that different sizes of Pd sites were being synthesized in each reflux, we expected that this difference would affect the distribution of Pd within the pores and on the surface of SOMS. Particularly, smaller sized Pd nanoparticles that were synthesized would be more capable of entering the pores of SOMS and adhering to the surfaces within the pores than the larger sized Pd nanoparticles. The XPS results above demonstrate a support of our initial understanding

about how size of the Pd nanoparticles created would affect dispersion and adherence to SOMS. As well, these results verify that there are size based differences in the Pd sites created via our synthesis technique.

Finally, N_2 physisorption was carried out on each sample in order to demonstrate how the size of Pd nanoparticles affected their placement within SOMS. Specifically, BET and BJH methods were used to probe the amount of Pd located within the pores of SOMS by comparing the surface area and pore volume to as-delivered SOMS. As can be seen in Table 3, below, as the ratio of PVP to Pd is increased from 1:1 to 10:1, the pore volume that is occupied decreases from 29.58% to 9.65%.

Table 3: Numerical results from BET/BJH methods of 1:1 and 10:1 samples as compared to as-delivered SOMS.

	Bare SOMS	10 : 1	1 : 1
BET Surface Area (m^2 / g)	570.50	475.33	515.95
Pore Volume (cm^3 / g)	0.6521	0.4592	0.5892
Pore Occupancy (% Volume)	-	29.58	9.65
Pore Diameter (nm)	3.73	3.62	3.73

While a difference in Pd particle size synthesized in each catalyst was already in the XPS results above, XPS only analyzes the adherence of Pd sites to the surface of SOMS whereas N_2 Physisorption can probe the amount of Pd located within the pores of SOMS. It was anticipated that the higher ratio of PVP to Pd nanoparticles, which would be smaller, would be more easily able to enter the pores and result in a higher occupancy of available pore volume. The results above, in tandem with the XPS results, demonstrate this to be true. Thus, this further verified our expectations about the size and distribution of Pd nanoparticles on the surface and within the pores of SOMS. As well, this also helped further indirectly demonstrate the difference in Pd catalyst site size between each sample.

Kinetic Testing

Two different kinetic quantities were explored for both the 1:1 and 10:1 samples synthesized: Turnover Frequency (TOF) and rate of reaction. In addition to exploring these values for the first time using an animated support like SOMS, TOF and rate of reaction were explored as a function of catalyst site size. Prior to all kinetic tests being conducted in the flow reactor setup outlined in the Methodology section, a calibration curve was obtained in order to find the concentration profile of HCl during the reaction. This in turn was used to calculate the percent yield of HCl in the system. Solutions of known concentrations of diluted HCl were passed through the reactor system and the conductivity values were recorded. The relationship between the conductivity and concentration of chloride ions in solution was found to be linear. The results of this calibration curve may be found in Figure A1 in Appendix A.

Rate of Reaction

The first kinetic quantity that was explored was the rate of reaction and the associated rate orders for each reactant. Using Equation 1 as a guideline, these tests were done to determine the steady state rate constant, k, as well as the orders of reaction for TCE and hydrogen for the HDC of TCE reaction. 10% ethanol was used across all experiments as this has been previously demonstrated to induce the optimal amount of swelling and access to all Pd sites within SOMS [2]. As well, we did a set of tests to verify this by finding yield of HCl as a function of 0%, 5%, and 10% ethanol. The results of this test can be found in Figure A2 in Appendix A.

First, we varied the concentration of hydrogen in the system for a fixed concentration of TCE in methanol at 5000 PPM. Two separate tests were run for the 1:1 and 10:1 catalysts, wherein water was bubbled with hydrogen for 1.5 hours and 0.5 hours, respectively, for each sample. A graph demonstrating the percentage yield of HCl over time for each of the four experiments conducted to determine the effect of hydrogen on the rate of reaction can be found below in Figure 3. The results from Figure 3 as well as a numerical tabulation of results in Table 4 demonstrate a negligible difference observed between the steady state yield of HCl between 1.5 hours and 0.5 hours of bubbling for both samples.

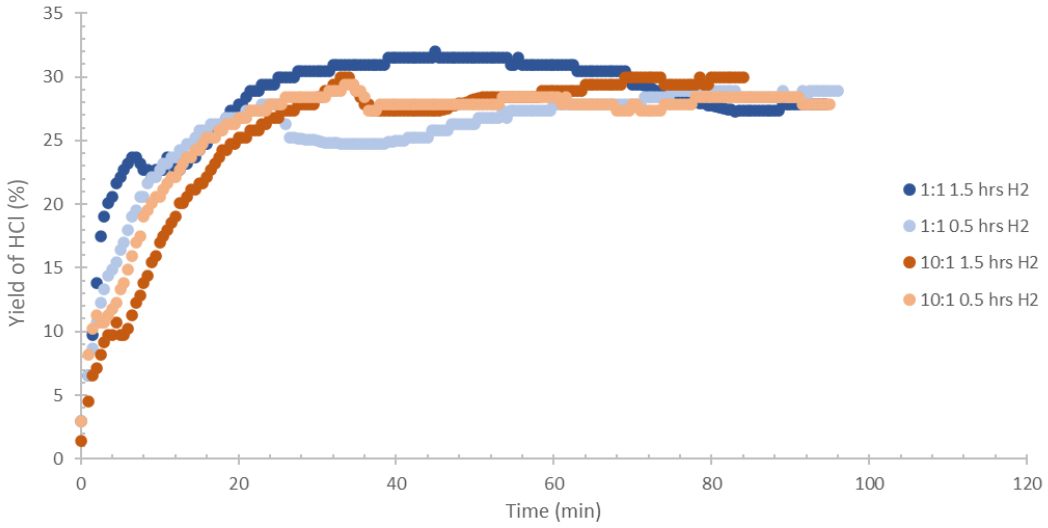


Figure 3: Yield of HCl over time for all of the variation of hydrogen experiments.

Table 4: Numerical results from the variation in hydrogen tests shown in Figure 3.

1.5 Hrs H2	Time to SS (min)	SS Value Yield HCl	SS dn/dt mol/min
1:1	27.0	29.91	4.74E-08
10:1	30.0	28.78	4.56E-08
0.5 Hrs H2	Time to SS (min)	SS Value Yield HCl	SS dn/dt mol/min
1:1	26.5	27.15	4.31E-08
10:1	27.5	28.09	4.45E-08

Comparing the time required to reach steady state, the percent yield of HCl, and the steady state formation of HCl in moles per minute for the above-mentioned experiments, there does not appear

to be a significant effect of hydrogen on any of these values. Thus, the reaction order with respect to hydrogen for the HDC of TCE under the current reaction conditions was found to be zero. Previous literature for both SOMS and conventional catalysts has demonstrated that the rate order for hydrogen for the HDC of TCE is zero, supporting the results found [16-17].

The next set of kinetic tests consisted of experiments with varying concentrations of TCE in the system for fixed hydrogen concentration at 1.5 hours of hydrogen bubbling. Two separate tests were run for the 1:1 and 10:1 catalysts, with 5000 ppm and 10000 ppm of TCE in methanol. Again, 10% ethanol was used for all experiments conducted. A graph demonstrating the percentage yield of HCl over time for each of the four experimented conducted to determine the effect of TCE concentration on the rate of reaction can be found below in Figure 4. The results from Figure 4 as well as numerical tabulation of results in Table 5 indicate that for both 1:1 and 10:1 samples that an increase in concentration of TCE in the experiment resulted in an overall greater formation of HCl at steady state.

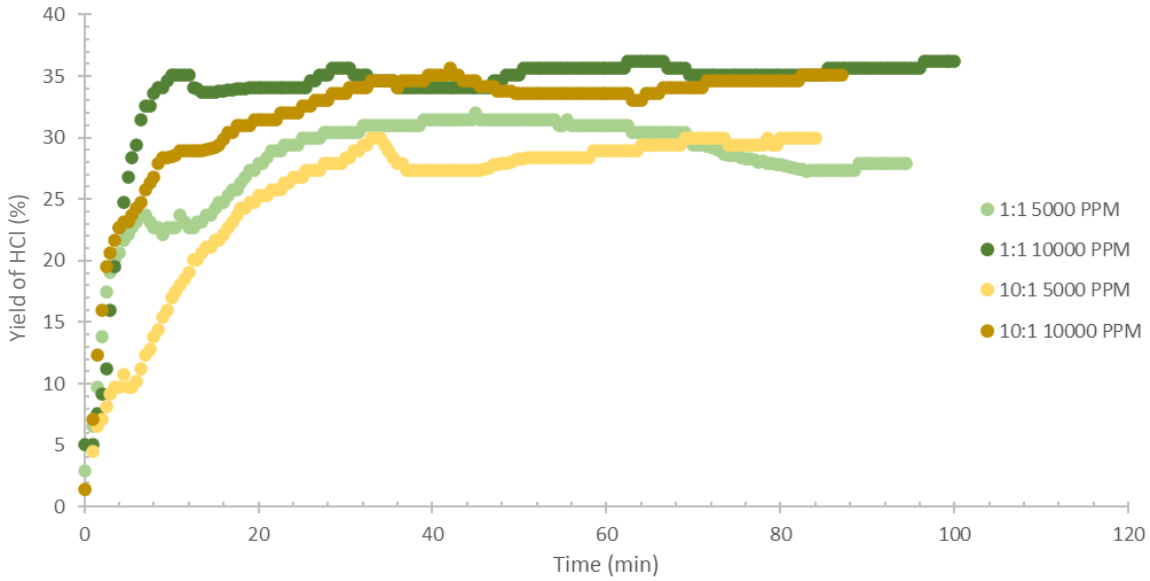


Figure 4: Yield of HCl over time for all of the variation of TCE experiments.

Table 5: Numerical results from the variation in TCE tests shown in Figure 4.

5000 PPM TCE	Time to SS (min)	SS Value Yield HCl	SS dn/dt mol/min
1:1	27.0	29.91	4.74E-08
10:1	30.0	28.78	4.56E-08
10000 PPM TCE	Time to SS (min)	SS Value Yield HCl	SS dn/dt mol/min
1:1	12.5	35.06	1.11E-07
10:1	27.5	34.21	1.08E-07

Looking first at the moles per minute of HCl formed at steady state for all experiments, there is a noticeable increase in HCl formed at 10000 PPM TCE as compared to 5000 PPM TCE feeds. Using the values obtained from the experiments, the rate order with respect to TCE for the HDC of TCE was found to be 1.23 and 1.24 for 1:1 and 10:1 samples, respectively. Thus, we would conclude that TCE follows roughly first order kinetics for the HDC of TCE, which is again corroborated by previous literature. [16-17, 23] Using the values of rate order determined for TCE for each of the catalyst samples, as well as the findings that the rate order with respect to hydrogen is zero, the rate constants for the rate of reaction equations were calculated and can be found below in Equations 4 and 5. The similarities in the value of rate constants between these equations demonstrates that size of Pd catalyst sites does not appear to have an effect on the yield of HCl in the HDC of TCE reaction.

$$\left(\frac{dn_{HCl}}{dt}\right)_{1:1} = \frac{0.298}{min} * [H_2]^0[TCE]^1 \quad (4)$$

$$\left(\frac{dn_{HCl}}{dt}\right)_{10:1} = \frac{0.287}{min} * [H_2]^0[TCE]^1 \quad (5)$$

Turnover Frequency

The second kinetic quantity that was explored was the TOF for each catalyst site size. Using Equation 2 as a guideline, TOF has one kinetically derived component and one derived via physical characterization of the catalyst being studied. To determine the steady state molar formation of

HCl required in the calculation of the TOF for each catalyst, we used a combination of experimental results gathered from the experiments used to determine rate of reaction. First, we graphed the activity curves for both the 1:1 and 10:1 samples carried out under 5000 PPM TCE in methanol, 1.5 hours of hydrogen bubbling, and 10% ethanol conditions. The graph of these curves may be found in Figure A3 in Appendix A Then, using the same strategy as before, we derived the steady state conversions for each of these reactions which can be found below in Table 6.

Table 6: Numerical results from the tests used to determine steady state formation of HCl for TOF.

	Time to SS (min)	SS Value Yield HCl	SS dn/dt mol/min
1:1	27.0	29.91	4.74E-08
10:1	30.0	28.78	4.56E-08

As can be seen in Table 6, there is effectively no difference in the steady state yield of HCl between the 1:1 and 10:1 samples. This, however, does not correlate with literature that has previously demonstrated the HDC of TCE to be a structure sensitive reaction [24-27]. The HDC of TCE reaction has been shown to be influenced by the type of support that a Pd catalyst is grown on as this has a direct effect on the ratio of Pd^0 to Pd^{2+} sites created which in turn affects TCE conversion [26-28]. While Transmission Electron Microscopy (TEM) or CO Chemisorption studies have previously been used to probe for this ratio of Pd^0 to Pd^{2+} sites in a catalyst, the usage of an animated support like SOMS complicates the ability to conduct these studies due to the need to maintain saturation in organic solvents for SOMS to stay swollen. An additional point that further complicates the usage of techniques like TEM or CO Chemisorption studies on these catalysts that were synthesized was the presence of the capping agent PVP.

PVP was used in the modified synthesis technique in this study to act as a binding agent to Pd which would prevent agglomeration of Pd nanoparticles in solution at these active sites. It has been

shown in literature that as PVP binds to the surface of Pd nanoparticles, the molecule attaches to electron rich Pd sites such as Pd^0 [29]. In addition to decreasing the amount of Pd^0 sites on the surface of Pd due to direct binding, the relatively high polarity of the C-N-C bond within PVP draws electrons away from the Pd surface surrounding the attachment creating many electron deficient Pd^{2+} sites from Pd^0 ones [29]. Given that these Pd^0 sites are the sites responsible for the binding of hydrogen from solution to carry out the HDC of TCE solution, a decrease in overall Pd^0 sites available directly leads to a decrease in reactivity [30]. Thus, based on the literature results we would expect that smaller Pd nanoparticles created in synthesis, which would require a greater amount of PVP capping agents to prevent agglomeration, would demonstrate a lower ratio of active Pd^0 to inactive Pd^{2+} sites and convert less TCE overall. However, literature has also demonstrated that at sufficiently high concentrations of PVP relative to binding sites which can accept PVP, Pd nanoparticles can form a loosely adhered coating of PVP on the surface which not only acts to prevent further PVP adherence via steric hinderance, but may also inhibit surface reactions from occurring at maximal rates [29].

Based on the similarity in steady state conversion of TCE as noted in Table 6, as well as the literature discussing the adherence of PVP in excess during synthesis, it is believed that the two samples that were synthesized were both sufficiently saturated with excess PVP and created a loosely bound coating around the catalyst sites that prevented a differentiation in catalytic results. Much like with the aforementioned difficulties surrounding the characterization of Pd sites, characterization of the PVP structures within each of the samples created were hindered by the animated nature of SOMS. As well, partial or complete removal of PVP from the surface of Pd sites for SOMS was also hindered due to the methods used requiring either heat that was sufficiently high enough to degrade the SOMS surface or required solvents such as tert-butylamine

which carry severe safety hazards [31-32]. As a result of the literature demonstrating a deviation from expectation of steady state conversion results, physical characterization of these samples for TOF was not explored.

Conclusion

This study has demonstrated a modified synthesis technique which can be used to synthesize size-controlled catalyst sites on the animated material, SOMS, which has not been attempted prior. The different sizes of catalyst sites synthesized were verified through a series of characterization steps. Additionally, attempts were made to explore the kinetics of the HDC of TCE not only within an animated material like SOMS for the first time, but with respect to differing sizes of Pd catalyst sites. While the rate orders with respect to hydrogen and TCE were found to follow results previously demonstrated in literature, the kinetic studies carried out did not demonstrate site specificity of the HDC of TCE reaction. It was determined that the likely cause of these issues was a combination of an excess of PVP capping agents used and a difficulty with conventional characterization techniques due to the unique features of SOMS. Further attempts to both characterize these materials and derive kinetic results that demonstrate site specificity will require an exploration of means of removal of some or all PVP capping agents in the samples synthesized.

Future Work

The first hurdle that must be overcome in the further studying of the kinetics of size controlled Pd-SOMS samples is a partial or total removal of PVP capping agents post synthesis. While some methods have been established in literature, an adaptation of one or more will likely be necessary to work around the unique features of the SOMS material. After successful removal of some or all PVP sites, kinetic experiments could continue in a similar fashion to the ones conducted in this study. As well, characterization techniques such as TEM and CO chemisorption may also need to

be adapted in order to further characterize both the Pd sites and PVP surrounding those sites in the size controlled Pd-SOMS catalysts.

Summary

An attempt was made to synthesize size controlled Pd catalyst sites within the pores of an animated support known as SOMS and then to kinetically characterize them. After modifying a synthesis technique to synthesize various sizes of Pd sites, conversion of TCE via the HDC of TCE reaction over these catalysts was carried out with some difficulty in obtaining results. Further probing of literature suggests that while the synthesis technique was successful, removal of the capping agent PVP used in the synthesis by some currently unknown means will be required before further kinetic experiments are conducted.

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Appendix A: Figures

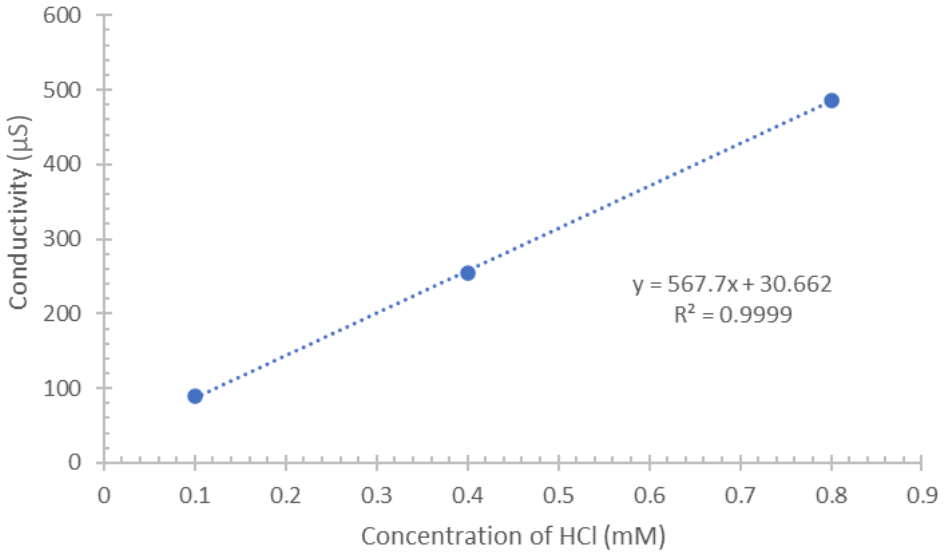

Figure A1: Calibration curve for the calibration of flow reactor tests.

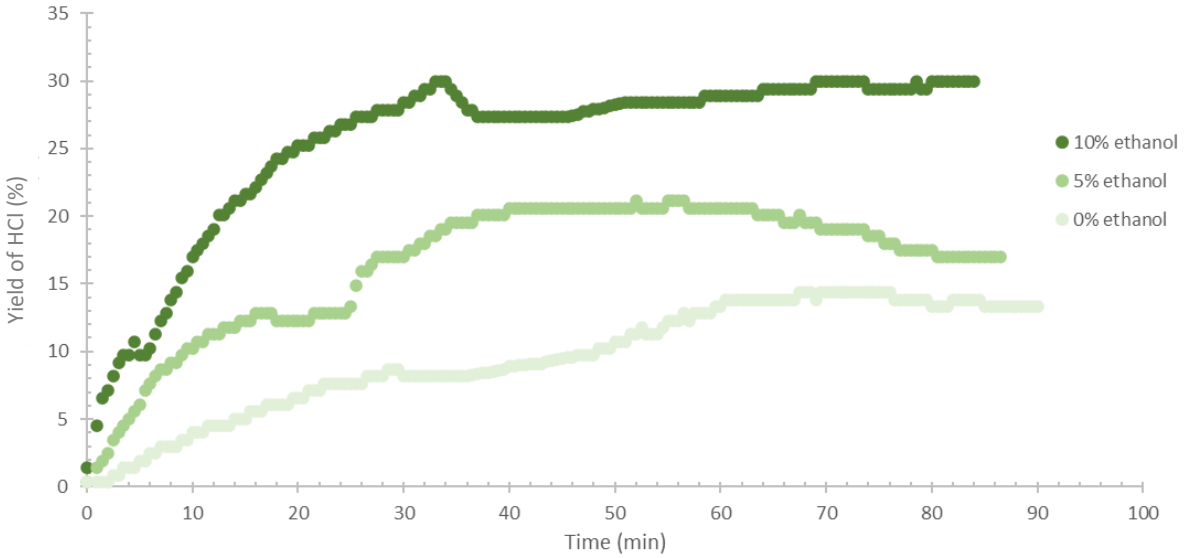

Figure A2: Verification of 10% ethanol as optimum concentration of ethanol for TCE conversion in 10:1 sample.

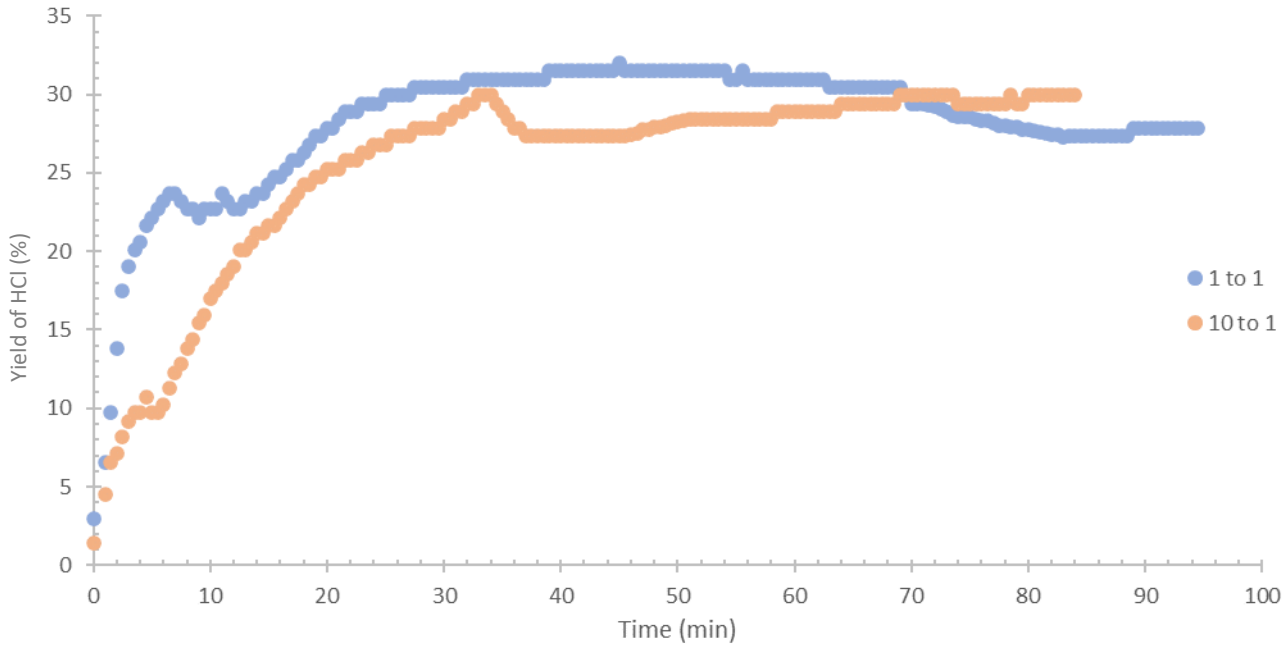

Figure A3: Yield of HCl over time for 1:1 and 10:1 catalysts with 5000 PPM TCE, 1.5 hours of H2 bubbling, and 10% ethanol.